

# PATENT SPECIFICATION

(11) 1 512 080

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(21) Application No. 30873/75 (22) Filed 23 July 1975  
 (31) Convention Application No. 49/084902  
 (32) Filed 24 July 1974 in  
 (33) Japan (JP)  
 (44) Complete Specification published 24 May 1978  
 (51) INT CL<sup>2</sup> G03C 1/00//F16C 13/00  
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 C4C2BX C4C5C C6



(54) LIGHT-SENSITIVE PRINTING PLATE  
 PRECURSOR

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a light-sensitive printing plate precursor.

When a light-sensitive printing plate precursor is exposed through an original image, it is usual practice to bring the original image into

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light-sensitive layer and one or more other layers, the uppermost layer being of a resin which is removable on development and the layer being formed from a viscous coating composition which is applied using a roller having an uneven patterned rolling surface, the coating being sufficiently viscous as to retain the uneven pattern imparted by the roller until the coating has dried.

The term "light-sensitive printing plate precursor" as used herein includes precursors of for example a lithographic printing plate, a letter-press printing plate and an intaglio

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## ERRATUM

### SPECIFICATION No. 1,512,080

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 45      erty comprises coating a support with a

these supports depending upon the type of  
 the printing plate. For example, in the case  
 of a lithographic printing plate, an aluminum  
 plate and a composite sheet in which an  
 aluminum sheet is provided on a polyethylene  
 terephthalate film as described in Japanese  
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## (54) LIGHT-SENSITIVE PRINTING PLATE PRECURSOR

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a light-sensitive printing plate precursor.

When a light-sensitive printing plate precursor is exposed through an original image, it is usual practice to bring the original image into firm contact with the surface of the light-sensitive side of the precursor, by compressing the precursor and the original image between a rubber sheet and a press glass and evacuating the space between the rubber sheet and the press glass. This is known as the vacuum contact method.

Since conventional light-sensitive printing plate precursors have a smooth surface, when the original image is applied to this surface using the vacuum contact method, the contact begins from the periphery. Thus, the centre portion is effectively sealed off and contact thereat is unreliable, unless an extremely prolonged evacuation is performed. If an imagewise exposure is made while the contact is still incomplete, the resulting image on the printing plate is fuzzy where the contact is incomplete.

In our British Patent Specification No. 1,495,361, we have proposed a light-sensitive printing plate precursor having a superficial matt layer removable upon development, whereby vacuum contact can be completed much faster without adversely influencing the properties of the printing plate. We proposed that this layer could be provided by using a coarse matting agent in the removable matt layer of the precursor, but we have now discovered that an advantageous process of producing a light-sensitive printing plate precursor having this fast vacuum contact property comprises coating a support with a

light-sensitive layer and one or more other layers, the uppermost layer being of a resin which is removable on development and the layer being formed from a viscous coating composition which is applied using a roller having an uneven patterned rolling surface, the coating being sufficiently viscous as to retain the uneven pattern imparted by the roller until the coating has dried.

The term "light-sensitive printing plate precursor" as used herein includes precursors of for example a lithographic printing plate, a letter-press printing plate and an intaglio printing plate. These precursors comprise essentially a support bearing a light-sensitive layer.

Suitable supports are those dimensionally stable plates which have been hitherto used as supports for printing plates. These supports include paper, synthetic resin (for example, polyethylene, polypropylene, polystyrene, and the like) laminated paper, plates of metals such as aluminum (including aluminum alloys), zinc, iron, copper, and the like, films of synthetic resin such as cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetal, and the like, and the above described metals such as aluminum, aluminum alloys, zinc, iron, and copper, laminated or vapor-deposited on a paper or a synthetic resin film. A suitable support can be selected from these supports depending upon the type of the printing plate. For example, in the case of a lithographic printing plate, an aluminum plate and a composite sheet in which an aluminum sheet is provided on a polyethylene terephthalate film as described in Japanese Patent Publication No. 18327/1973 are preferred. In the case of a letterpress printing plate, a polyethylene terephthalate film, an aluminum plate or an iron plate, are preferred.



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SEE ERRATA SLIP

The support is subjected to a surface-treatment, if desired. For example, in the case of the lithographic printing plate, a treatment to render the surface hydrophilic is applied to the surface of the support. There are various kinds of treatments to render the surface hydrophilic. For example, in the case of a support with a synthetic resin surface, the so-called surface treatments such as a chemical treatment, a discharge treatment, a flame treatment, an ultraviolet light treatment, a high frequency treatment, a glow discharge treatment, an active plasma treatment, a laser treatment, and the like as described in, for example, U.S. Patents Nos. 2,764,520, 3,497,407, 3,145,242, 3,376,208, 3,072,483 3,475,193, 3,360,448 and British Patent No. 788,365, and a method comprising coating an undercoating layer on the synthetic resin surface after the above surface-treatment can be employed.

Various arrangements of layers are known. For example, a multilayer method in which a hydrophobic resin layer capable of adhering to synthetic resins and having good solubility in a coating solvent is coated as a first layer and a hydrophilic resin layer is coated as a second layer, and a single layer method in which a layer of a resin containing hydrophobic and hydrophilic groups in the same polymer is coated can be used.

With a support having a metal surface, particularly an aluminum surface, preferably a surface treatment such as a graining treatment such as sand-grinding, an immersion treatment using an aqueous solution of sodium silicate e.g., as described in U.S. Patent 2,714,066, potassium fluorozirconate, e.g. as described in U.S. Patent 2,946,683, a phosphate e.g., as disclosed in U.S. Patents 3,030,212 and 3,808,000, or an anodic oxidation treatment is employed e.g. as described in U.S. Patents 3,030,212 and 3,808,000. An aluminum plate subjected to an immersion treatment using a solution of sodium silicate in water after graining as described in U.S. Patent No. 2,714,066, and an aluminum plate subjected to an immersion treatment using a solution of an alkali metal silicate in water after an anodic oxidation treatment as described in U.S. Patent No. 3,181,461 are preferably used. The above anodic oxidation treatment can be carried out by passing electricity through an electrolyte comprising one or more aqueous or non-aqueous solutions of inorganic acids such as phosphoric acid, chromic acid, sulphuric acid, boric acid, or organic acids such as oxalic acid, sulfamic acid, or the salts thereof, using an aluminum plate as the anode.

Silicate electro-deposition as described in U.S. Patent No. 3,658,662 is also useful as a hydrophilic treatment of an aluminum surface.

These treatments to render the surface hydrophilic are carried out in order to prevent adverse interactions between the surface of the support and the light-sensitive composition provided on the surface, and to increase the adhesion of the light-sensitive layer to the surface as well as to render the surface of the support hydrophilic.

Suitable light-sensitive materials which can be provided on the support include any materials provided that the solubility and swelling property in a developer of the material before and after exposure is different. Preferred light-sensitive materials are diazo compounds such as a light-sensitive composition comprising a diazo resin and shellac (e.g., as disclosed in Japanese Patent (OPI) No. 2440/1972), a homo- or co-polymer of hydroxyethyl methacrylate and a diazo resin, a diazo resin and a soluble polyamide (e.g., as disclosed in U.S. Patent No. 3,751,257), an azide light-sensitive material and an epoxy resin (e.g., as disclosed in U.S. Patent No. 2,852,379), an azide light-sensitive material, a diazo resin, light-sensitive resins which contain unsaturated double bonds in the molecule and which undergo a dimerization reaction upon irradiation with activating radiation, becoming insoluble, a typical example of which is polyvinyl cinnamate, polyvinyl cinnamate derivatives such as are described in, for example, British Patent Nos. 843,545, 966,297, and U.S. Patent No. 2,725,372, light-sensitive polyesters produced by the condensation of bisphenol A and divanillacyclohexanone, and *p*-phenylenedioxy acrylate and 1,4 - di- $\beta$  - hydroxyethoxycyclohexanone as described in Canadian Patent No. 696,997, prepolymers of diallylphthalate as described in U.S. Patent No. 3,462,267, ethylene-based unsaturated compounds containing at least two double bonds in the molecule and capable of undergoing a polymerization reaction upon irradiation with activating radiation such as unsaturated esters of polyols as described in Japanese Patent Publication No. 8495/1960, e.g., ethylene di(meth)acrylate, diethylene-glycol di(meth)acrylate, glycerol di(meth)-acrylate, glycerol tri(meth)acrylate, ethylene di(meth)acrylate, 1,3 - propylene di(meth)-acrylate, 1,4 - cyclohexanediol (meth)-acrylate, 1,4 - benzenediol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, 1,3 - propyleneglycol di(meth)acrylate, 1,5 - pentane-diol di(meth)acrylate, pentaerythritol tri(meth)acrylate, bisacrylates or methacrylates of polyethylene glycol having a molecular weight of about 50 to 500, unsaturated amides, particularly amides of  $\alpha$  - methylene carboxylic acids and amides of  $\omega$  - diamines in which  $\alpha,\omega$  - diamines and carbon are present therebetween such as methylene bis(meth)acrylamide and diethylenetriamine tris(meth)acrylamide and divinyl succinate, divinyl adipate, divinyl phthalate, divinyl tere-

phthalate or divinylbenzene - 1,3 - disulphonate. Light-sensitive compositions comprising these light-sensitive materials and binders such as polyvinyl alcohol, polyvinyl hydrogen phthalate, cellulose derivatives containing carboxy groups in their side chains such as carboxymethyl cellulose or a copolymer of methyl methacrylate and methacrylic acid are useful as negative working type light-sensitive compositions which become insoluble due to actinic irradiation.

Light-sensitive compositions comprising those light-sensitive materials as described in U.S. Patents Nos. 3,635,709, 3,061,450, 3,061,120, *o* - diazooxide based light-sensitive materials, phosphotungstates of a diazo resin (e.g., as described in Japanese Patent Publication No. 7663/1964), a yellow potassium ferrocyanide of a diazo resin (e.g. as disclosed in U.S. Patent No. 3,113,023), and a diazo resin and polyvinyl hydrogenphthalate are useful as positive-working type light-sensitive materials.

Light-sensitive compositions containing linear polyamides as described in U.S. Patents Nos. 3,081,168, 3,486,903, 3,512,971 and 3,615,629, and monomers containing addition-polymerizable unsaturated bonds are also useful.

A suitable application rate for the light-sensitive layer is from 0.01 g/m<sup>2</sup> to 7 g/m<sup>2</sup>, preferably 0.1 g/m<sup>2</sup> to 5 g/m<sup>2</sup> (dry weights). The resin layer may be provided on the light-sensitive layer, for example to give a material as described in U.S. Patent No. 3,136,637; those light-sensitive printing plate precursors comprise a support, a light-sensitive layer on the support, and an oleophilic, hydrophobic, water-insoluble, and solvent-softenable resin layer on the light-sensitive layer; when such a light-sensitive printing plate precursor is exposed to light through an original image, the exposed areas of the light-sensitive layer are rendered insoluble in a developer, and at the same time, combine with the resin layer thereon, whereas the unexposed areas of the light-sensitive layer are not changed and are soluble in the developer. Thus if this light-sensitive layer is developed, the unexposed areas are dissolved in and removed by the developer penetrating through the resin layer thereon. Therefore, if the surface is slightly rubbed with a fibrous pad, e.g. of cotton, dampened with the developer, the resin layer on the unexposed areas is removed, whereas the exposed areas of the light-sensitive layer and the resin layer on the exposed areas are not affected by the developer and remain on the support, whereby a printing plate having a clear image thereon can be obtained.

In accordance with the process according to the invention, the layer forming the uppermost layer of the light-sensitive printing plate precursor is applied by roller-coating, the roller having an uneven rolling surface. The precursor may furthermore have an additional oleophilic, hydrophobic, water-insoluble and solvent-softenable resin layer, the light-sensitive layer on which the aforesaid uppermost resin layer is applied with the roller having an uneven surface. Suitable examples of such additional oleophilic, hydrophobic, water-insoluble and solvent-softenable resins which can be used are disclosed in U.S. Patents Nos. 3,522,042 and 3,622,331.

The coating roller for applying the uppermost layer can be made from various materials. Preferred materials include polytetrafluoroethylene, polyethylene, polyvinyl chloride, similar synthetic resins, carbon fibre and metals such as stainless steel.

The depressions and/or projections on the surface of the coating roller can have various forms, such as cones, hexagonal prisms, cuboids, cubes, pyramids, triangular prisms, part-spheres and cylinders. The projections and depressions can either all have the same form, or have various forms. The average radial distance from the surface of the roller to the top of a projection or to the bottom of a depression (hereinafter referred to merely as "depth") can suitably be from 50 nm to 100  $\mu$ , with a preferred range being from 1 to 50  $\mu$ . Where the depth is less than 50 nm, the effect obtained when a decreased vacuum contacting period is used is reduced, whereas where the depth is above 100  $\mu$ , the closeness of the contact between the original image and the light-sensitive printing plate tends to be insufficient, thereby reducing the sharpness of the printing plate. A suitable distance between adjacent projections and depressions ranges from 0.01 to 20 mm, with a preferred range being from 0.1 to 1 mm. As in the case of the depth, where the distance is over 20 mm, a lesser effect is obtained when a decreased vacuum contacting period is used, whereas where the distance is under 0.01 mm, the closeness of contact between the original image and the light-sensitive printing plate becomes insufficient, thereby resulting in a reduction in the sharpness of the printing plate.

Where the projection has the form of a column, the suitable diameter is from 0.005 to 10 mm, and preferably from 0.05 to 0.5 mm.

In a particularly preferred embodiment of the present invention, a resin layer capable of dissolving in the developer for the light-sensitive material of the printing plate or capable of being removed by peeling is provided as the upper layer of the printing plate precursor, and the resin layer is applied using the above described coating roller with an uneven surface. Suitable resins for the aforesaid removable layer can be selected depending upon the developer to be used. Representative examples of these resins are gum

arabic, glue, casein, celluloses such as cellulose xanthate, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropoxymethyl cellulose or carboxymethyl cellulose, starches such as soluble starch or modified starch, polyvinyl alcohol, polyethylene oxide, polyacrylic acid, polyacrylamide, polyvinyl methyl ether, an epoxy resin, a phenol resin (a novolak-type phenol resin being preferred), polyamides (including those polyamides soluble in alcohols containing 1 to 6 carbon atoms such as methanol, ethanol, isopropanol, butanol, t - butanol, pentanol or hexanol), a polystyrene sulphonic acid salt or polyvinyl butyral. These resins can be used individually or as mixtures comprising two or more thereof.

The resin layer as described above is preferably in a dry weight of say 0.01 to 1 g/m<sup>2</sup>, preferably 0.2 to 0.5 g/m<sup>2</sup>.

The vacuum contacting period can be further shortened by incorporating a matting agent into the resin layer. Typical matting agents include silicon dioxide, zinc oxide, titanium oxide, zirconium oxide, glass particles, alumina, starch, polymer particles such as particles of polymethyl methacrylate, polystyrene or a phenol resin, and those matting agents described in U.S. Patents Nos. 2,701,245 and 2,991,101. These matting agents can be used individually or in admixture with each other. A suitable amount of the matting agent is from 0.03 to 4 parts, preferably 0.3 to 2 parts, per part by weight of the binder.

Since the uppermost layer of the light-sensitive printing plate precursor produced by the process of the invention is a resin layer capable of dissolving in the developer, a printing plate produced from the precursor is completely unaffected by the resin layer since that is wholly removed before printing.

A printing plate produced from a precursor according to the invention has a slightly lower print-durability than that produced from a precursor in which the resin layer is provided with a roller having a smooth surface, but the development rate of such a material is increased. The reason for this is believed to be that the contact area between the resin layer and the developer increases since the resin layer is matted, and thus the developer penetrates through the resin layer more rapidly, thereby reaching the light-sensitive layer more rapidly. A matting agent as described above can be incorporated into this resin layer.

The superficial matting of the light-sensitive printing plate precursor necessitates no special techniques for imagewise exposure. A precursor produced according to the present invention is less damaged by other precursors, and when the precursors are superposed, they

do not come into close contact with each other. Also, vacuum-contact to an original through which the precursor is to be exposed is rendered more reliable and speedy.

The invention extends to a printing plate comprising an imagewise exposed precursor as set forth above, which has been developed, and to printed matter obtained from an inked printing plate as set forth.

The present invention is explained in greater detail by reference to the following examples. All parts, percentages and ratios are by weight unless otherwise indicated.

#### EXAMPLE 1

A 0.3 mm thick aluminum plate was subjected to a degreasing treatment by dipping the plate in a 10% solution of sodium triphosphate in water at 80°C for 3 minutes, washing with water, and dipping in 70% nitric acid. After water-washing, the aluminum plate was dipped in a 2% solution of potassium fluorozirconate in water at 80°C for 3 minutes, washed with water, and dried. On the aluminum plate so treated was coated a solution having the following composition to provide a light-sensitive layer. The coating amount was 500 mg/m<sup>2</sup> on a dry basis.

2 - Diazo - 1 - naphthol - 5 - sulfonate with a polyhydroxyphenyl condensation product of pyrogallol and acetone) described in Example 1 of U.S. Patent 3,635,709)	95
Cyclohexane	5 g 80 g

On this light-sensitive layer, a solution having the following composition was coated in a dry weight of 0.3 g/m<sup>2</sup> and dried.

Water	100 g
Hydroxypropoxymethyl Cellulose (degree of hydroxypropoxylation: 7 to 12 mole %; degree of methylation: 28 to 30 mole %)	105
	30 g

This layer was provided using a roller having an uneven surface in which the distance between the projections and depressions was 0.1 to 1 mm, the depth was 1 to 5  $\mu$ , and the projections had the form of a cylinder having a radius of 0.05 mm. With the light-sensitive printing plate so produced, the time required for bringing the plate into close contact with an original image in accordance with the vacuum contacting method was measured, and the results obtained are shown in Table 1 below. The coating amount was 0.3 g/m<sup>2</sup> on a dry basis.

TABLE 1

Distance between Projections and Depressions (mm)		Depth of Depressions ( $\mu$ )	Time Required for Close Contact (seconds)
5	0.1	1	40 to 30
	0.1	3	20 to 15
	0.5	2	20 to 15
	0.5	5	10 to 12
	1	3	10 to 12
	1	5	10 to 12
Not coated			More than 60

It is evident from the above results that the time required for bringing the plate into close contact with an original image can be markedly shortened by using the light-sensitive printing plate of the present invention.

Each light-sensitive lithographic printing plate was exposed to light using a 35 ampere carbon arc lamp at a distance of 70 cm for 2 minutes and then developed by dipping the exposed plate in a 5% solution of sodium triphosphate in water for 1 minute and by rubbing the surface gently with absorbent cotton. The hydroxypropylmethyl cellulose layer was completely dissolved and removed over the entire area of the plate, and further the exposed areas of the light-sensitive layer were removed whereby a positive image corresponding to the original image was obtained. All printing plates had equal printing properties. That is, no effect on printing capabilities due to the provision of the resin layer on the light-sensitive printing plate was observed.

#### EXAMPLE 2

The procedures of Example 1 were repeated wherein a solution having the following composition was coated in a dry weight of 0.3 g/m<sup>2</sup> as the resin layer.

Water	100 g
Polyvinyl Alcohol	25 g

The distance between the cylindrical projections and depressions, the depth, and the radius of the projections of the roller and the coating amount on a dry basis of the resin were 0.5 mm, 5  $\mu$ , 0.05 mm, and 0.5 g/m<sup>2</sup>, respectively. With the light-sensitive lithographic printing plate so produced, the time required for bringing the plate into close contact with an original image, in a vacuum contacting method, was 10 to 15 seconds. In the same manner as in Example 1, a printing plate was produced from this light-sensitive lithographic printing plate and the printing capabilities of the plate were measured. Substantially the same results as obtained in Example 1 were obtained.

#### EXAMPLE 3

A 0.3 mm thick aluminum plate was degreased by dipping the plate in a 10% solution of sodium triphosphate in water at 80°C for 1 minute, and washed with water. The aluminum plate was grained by rubbing the surface of the plate with a nylon brush while flowing a liquid with pumice dispersed therein over the plate. After sufficient water-washing, the aluminum plate was dipped in a 5% solution of JIS No. 3 sodium silicate ( $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  the molar ratio of which could vary over the range 3.1 to 3.3) at 75°C for 3 minutes. After sufficient water-washing and drying, a viscous solution having the following composition was coated in a dry amount of 1 g/m<sup>2</sup> and dried to provide a light-sensitive layer.

	Amount (g)	
Shellac	10	
Polyvinyl Acetate	1	
Condensate of 4 - Diazo - 4' - methoxydiphenylamine Hexa-fluorophosphate and Formaldehyde	80	
Methylene Blue	0.3	
Methanol	200	85
Furfuryl Alcohol	50	
Polyvinyl Pyrrolidone	50 g	90
Chloroform	100 g	

On the thus prepared light-sensitive layer was coated and dried a solution having the following composition.

The distance between the adjacent projections and depressions, the dry coating amount and the depth and the radius of the cylindrical projections on the roller were 1 mm, 0.3 g/m<sup>2</sup>, 3  $\mu$ , and 0.1 mm, respectively. With the thus prepared light-sensitive lithographic printing plate, the time required for bringing the plate into close contact with an original image in a vacuum contacting method was 15 to 20 seconds. On the other hand, with a light-sensitive printing plate on which the above resin layer was not provided, the time required for bringing the plate into close contact with the original image was more than 60 seconds.

The light-sensitive lithographic printing plate closely contacted with the original image was exposed to light from a 30 ampere carbon arc lamp at a distance of 70 cm for 5 minutes. This plate was developed by dipping the plate in a developer having the following composition for 10 seconds and then by rubbing the surface of the plate with a soft cloth.

10	Methanol	10 g
	Water	80 g
	Sodium Hydroxide	1 g

The resin layer was dissolved and removed, and further the unexposed areas of the light-sensitive layer were completely removed whereby a printing plate was obtained. The thus produced printing plate had substantially the same capabilities as a printing plate produced from a light-sensitive printing plate with no resin layer.

#### EXAMPLE 4

On a surface-treated aluminum plate as described in Example 1 was coated a solution having the following composition in a dry weight of 0.12 g/m<sup>2</sup> and dried to provide a light-sensitive layer.

30	Condensate of <i>p</i> - Diazodiphenylamine <i>p</i> - Toluenesulfonate and Formaldehyde	1 g
	Ethylen Dichloride	100 g

Methanol 100 g

On this light-sensitive layer was coated a solution having the following composition.

35	Polyvinyl Formal	4 g
	Phthalocyanine Blue	1 g
	Ethylen Dichloride	500 g
	Monochlorobenzene	20 g

The weight after drying when combined with the weight of the light-sensitive layer was 0.31 g/m<sup>2</sup>. On this layer was coated, using a roller having an uneven surface, a viscous solution having the following composition, and the coating was dried.

45	Water	100 g
	Hydroxypropylmethyl Cellulose (the same as described in Example 1)	50 g

The distance between the projections and depressions, the dry coating amount and the depth and the radius of the cylindrical projections on the roller were 0.5 mm, 0.4 g/m<sup>2</sup>, 5  $\mu$ , and 0.2 mm, respectively.

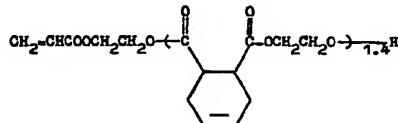
The thus obtained light-sensitive printing plate could be closely contacted with an original image in a vacuum contacting method in 10 to 12 seconds. On the other hand, with a light-sensitive printing plate on which the

above resin layer was not provided, the time required for bringing the plate into close contact with an original image was 60 to 70 seconds.

The light-sensitive printing plate brought into close contact with the original image was exposed to light from a 35 ampere carbon arc lamp at a distance of 70 cm for 1 minute, and the plate was then developed by dipping in a developer of isopropyl alcohol/water=2:1 (volumetric ratio) at 20°C for 1 minute and by lightly rubbing the surface with absorbent cotton. The resin layer was removed over the entire area of the plate, and further the unexposed areas of the light-sensitive layer and the polyvinyl formal layer lying on the areas were completely removed, whereas the exposed areas of the light-sensitive layer and the polyvinyl formal layer lying thereon remained without being damaged. This printing plate provided more than 50,000 sheets of good printings and thus had the same capability as a printing plate produced from a light-sensitive printing plate in which no resin layer was provided.

#### EXAMPLE 5

A mixture of 53 g (0.5 mole) of diethylene glycol and 197 g (1.05 mole) of xylylenediisocyanate was reacted at 80°C for 2 hours. To the reaction mass were added 390 g (1.0 mole) of hydroxyethyl tetrahydrophthalyl acrylate (OH value: 146; average molecular weight: 390) represented by the formula:



and 0.30 g of 2,6 - di - tert - butylresol as a polymerization inhibitor, and these materials were then reacted at 80°C for 8 hours while blowing air through the mixture to form a divinyl urethane compound.

To 60 parts of this divinyl urethane compound were added cellulose acetate hydrogen phthalate, CAP (trade name, produced by Wako Jyunyaku Co., phthalic acid content: 32% by weight), 1 part of benzoin ethyl ether as a sensitizer, 0.05 parts of 4,4 - thio-bis(3 - methyl - 6 - tert - butylphenol) as a thermal polymerization inhibitor, 0.025 parts of Methylene Blue as an image colorant, and 40 parts of acetone and 30 parts of methanol as solvents. The resulting solution was allowed to stand at 40°C for one day and night in order to defoam the mixture. The thus treated solution was coated on a 0.3 mm thick grained aluminum plate and dried to form a 0.6 mm thick light-sensitive layer thereon. On this light-sensitive layer was

coated, using a roller having an uneven surface, a viscous solution having the following composition in a dry weight of 1.5 g/m<sup>2</sup>, and the coating was dried.

5	Water	100 g
	Polyvinyl Alcohol	25 g

The distance between the projections and depressions, the dry coating amount, the radius of the projections, and the depth were 10 1 mm, 0.3 g/m<sup>2</sup>, 0.1 mm, and 2  $\mu$ , respectively.

The light-sensitive letterpress printing plate could be brought into close contact with an original image using a vacuum contacting method in 15 to 20 seconds. The printing plate was exposed to light with a printer equipped with 20-watt chemical lamps (FL-20 BL, produced by Tokyo Shibaura Electric Co., Ltd.) at 6 cm intervals for 10 minutes. Then this plate was developed by dipping the plate in a developer having the following composition.

25	Isopropanol	0.5 g
	Sodium Hydroxide	0.2 g
	Water	100 g

The resin layer was removed over the entire area of the plate, and further the unexposed areas of the light-sensitive layer were dissolved out whereby a good quality letterpress printing plate was obtained.

#### EXAMPLE 6

The procedure of Example 1 was repeated wherein a viscous solution having the following composition was coated using a roller having an uneven surface in a dry weight of 1.0 g/m<sup>2</sup> as an overcoating layer in place of the resin layer, and the coating was dried.

40	n - Propyl Alcohol	50 g
	Methanol	50 g
	Styrene - Maleic Acid Copolymer	25 g

The distance between the projections and depressions and the depth and the radius of the cylindrical projections on the roller were 0.3 mm, 2  $\mu$ , and 0.5 mm, respectively.

The time required for bringing the light-sensitive printing plate into close contact with an original image was 15 to 20 seconds. In the same manner as described in Example 1, a printing plate was produced from the light-sensitive printing plate precursor. This printing plate was slightly inferior to that provided with an evenly coated overcoating layer in printing durability, but the time for development was shortened with this printing plate.

#### WHAT WE CLAIM IS:—

1. A process for producing a light-sensitive

printing plate precursor, comprising coating a support with a light-sensitive layer and one or more other layers, the uppermost layer being of a resin which is removable on development and the layer being formed from a viscous coating composition which is applied using a roller having an uneven patterned rolling surface, the coating being sufficiently viscous as to retain the uneven pattern imparted by the roller until the coating has dried.

2. A process as claimed in Claim 1, wherein the light-sensitive printing plate precursor consists of the support, the light-sensitive layer on said support, and the resin layer on said light-sensitive layer.

3. A process as claimed in Claim 1 or 2, wherein the resin is gum arabic, glue, casein, a cellulose, a starch, polyvinyl alcohol, polyethyleneoxide, polyacrylic acid, polyacrylamide, polyvinyl methyl ether, an epoxy resin, a phenol resin, a polyamide, a polystyrene sulphonic acid salt, polyvinyl butyral or a mixture thereof.

4. A process as claimed in any preceding claim, wherein the resin layer has a dry weight of from 0.01 to 1 gram per square metre of the support.

5. A process as claimed in Claim 4, wherein said weight is from 0.2 to 0.5 g per square metre.

6. A process as claimed in any preceding claim, wherein the resin layer contains one or more matting agents.

7. A process as claimed in Claim 6, wherein the weight of matting agent in the resin layer is from 0.03 to 4 parts per part of the resin.

8. A process as claimed in Claim 7, wherein the weight of the matting agent in the resin layer is from 0.3 to 2 parts per part of the resin.

9. A process as claimed in any preceding claim, wherein the light-sensitive layer has a dry weight of from 0.01 to 7 g per square metre of the support.

10. A process as claimed in any preceding claim, wherein the light-sensitive layer has a dry weight of from 0.1 to 5 g per square metre of the support.

11. A process as claimed in any preceding claim, wherein the uneven rolling surface is of polytetrafluoroethylene, polyethylene, polyvinyl chloride, carbon fibre or stainless steel.

12. A process as claimed in any preceding claim, wherein the uneven rolling surface has projections and/or depressions such that the surface deviates from a pure cylinder by from 50 nanometres to 100 microns measured radially from the roller axis and wherein the distance between adjacent projections and depressions is 0.01 to 20 millimetres measured along the surface of the notional pure cylinder.

13. A process as claimed in Claim 12,

wherein the rolling surface deviates from a pure cylinder by from 1  $\mu$  to 50  $\mu$  measured radially.

14. A process as claimed in Claim 12 or 5 13, wherein the deviations from a pure cylinder occur over a distance of from 0.1 to 1 mm measured along the surface of the notional pure cylinder.

15. A process as claimed in any preceding 10 claim, wherein the rolling surface has depressions and/or projections in the form of any of cones, hexagonal prisms, cuboids, cubes, pyramids, triangular prisms, part-spheres and cylinders.

16. A process as claimed in any preceding 15 claim, wherein the rolling surface has cylindrical projections having a diameter of from 0.005 to 10 mm.

17. A process as claimed in Claim 16, 20 wherein the diameter of the cylindrical projections is from 0.05 to 0.5 mm.

18. A process of producing a light-sensitive printing plate precursor, substantially as hereinbefore described in any one of Examples 1 to 6 apart from comparative parts thereof.

19. A light-sensitive printing plate precursor produced by a process as claimed in any preceding claim.

20. A printing plate produced from a light-sensitive printing plate precursor as claimed in Claim 19, which precursor has been image-wise exposed and developed.

21. Printed matter obtained by printing from a printing plate as claimed in Claim 20, which plate has been inked.

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